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Solvothermal Approach to the Synthesis of Triangular Re(III) Iodide and Bromide Cluster Complexes

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Abstract—Crystalline Re_3I_9 (**1**) is formed in a quantitative yield upon the hydrothermal reaction of $NaReO_4$ with concentrated HI at 200°C. The reaction of Re_3I_9 with HBr at 200°C results in complete replacement of iodide ligands with bromide ligands with retention of the cluster core. The addition of pyridine to the reaction mixture leads to crystallization of the pyridinium salt $(PyH)_2[Re_3Br_{11}(H_2O)] \cdot 4H_2O$ (**2**). In the presence of phosphoric acid, $(PyH)_2[Re_3Br_9(PO_4H)]{\cdot}H_2O$ (**3**) and $(Et_4N)_2[Re_3Br_9(PO_4H)]{\cdot}2H_2O$ (**4**) were isolated. The crystal structures of the compounds **2**–**4** were determined by single crystal X-ray diffraction. Complexes **1** and **4** were characterized by powder X-ray diffraction. The Re/halogen ratio for compounds **1**–**4** was determined by energy dispersive spectroscopy. Elemental analysis and ^{31}P NMR spectroscopy data were obtained for compound **4**, and vibrational spectra were measured for **1** (far-IR range) and **4** (near-IR range). The data for thermal stability in inert atmosphere were obtained for **1**.

Keywords: clusters, iodides, bromides, rhenium, X-ray diffraction analysis, aqua complexes, phosphate complexes

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INTRODUCTION

Rhenium trihalides were obtained soon after the discovery of rhenium in the early 1930s [1], but their cluster nature was established only in the 1960s. According to X-ray diffraction data, ReX_3 (X = Cl, Br, I) contain triangular cluster groups $\{Re_3(\mu_2\text{-}X)_3\}^{6+}$ connected by halide bridges into layers (chloride, bromide) or into zigzag chains (iodide) and are described more adequately by the tripled formula Re_3X_9 [2–4]. The interpretation of short rhenium–rhenium distances as being due to the formation of a double bond between the metal atoms was a milestone in the development of the concept of clusters as a separate class of chemical compounds. This unusual bond situation (three metal–metal double bonds in a three-membered ring) is interpreted by theoreticians in different ways, either as a system with a high degree of aromaticity [5] or as a system with fully delocalized Re–Re π bonds [6]. The chemical properties of rhenium trihalide clusters were actively studied in the 1960s–1980s; this revealed examples of ligand substitution reactions without a change in the cluster core and reactions involving transformation of the cluster [7]. Later, it was found that Re_3X_9 trihalides are convenient building blocks and/or starting compounds for the preparation of rhenium chalcogenide and pnictide clusters [8–11]. Nevertheless, in our opinion, the chemical reactivity and synthetic potential of this interesting class of compounds have not been adequately studied. This is largely associated with the lack of convenient methods for large-scale synthesis of Re_3X_9. Analysis of the published methods of synthesis indicates that the least studied Re_3I_9 is the most readily accessible trihalide, while the preparation of chloride and bromide requires several steps [12]. Only Re_3Br_9 can be obtained by the direct synthesis from the elements; however, experimental conditions (heating at 600°C in a sealed tube for many days) are associated with the risk of explosion and preclude accumulation of large amounts of the product [13]. Here we propose an optimized procedure for the synthesis of crystalline Re_3I_9 and its conversion to bromide and its derivatives in quantitative yields.

EXPERIMENTAL

Commercially available chemicals ($NaReO_4$, HI, HBr, H_3PO_4, Et_4NBr, and pyridine) of at least analytical grade were used. IR spectra were measured on Scimitar FTS 2000 (4000–400 cm^{-1}) and Vertex 80 (600–100 cm^{-1}) Fourier transform infrared spectrometers. Energy dispersive X-ray (EDX) spectra were